JOURNAL OF SOLID STATE CHEMISTRY 77, 394–400 (1988)

Vibrational Spectra of $Te(OH)_6 \cdot 2NH_4H_2PO_4 \cdot (NH_4)_2HPO_4$

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Received April 11, 1988; in revised form August 2, 1988

The IR and (polarized) Raman spectra of $Te(OH)_6 \cdot 2NH_4H_2PO_4 \cdot (NH_4)_2HPO_4$ were recorded and analyzed. It was found that the hydrogen atoms are not strongly bonded to the oxygen atoms of phosphate groups and hence the phosphate ions exist as PO_4^{3-} ions rather than as HPO_4 and H_2PO_4 groups. The stretching and bending frequencies of PO_4 and NH_4 groups occupy a wide range of spectrum due to the presence of a large number of these groups in the unit cell. © 1988 Academic Press, Inc.

Introduction

Recently, several authors reported the structural and vibrational properties of crystals containing different anions (*1–3*). Liegeois-Duyckaerts and Tarte (*4*) performed vibrational spectroscopic analyses of the mixed crystals $A_2B^{II}B^{VI}O_6$ (A = Ba, Sr; B^{II} = Mg, Cd, Ca; and B^{VI} = Mo, W, Te) and inferred that the frequencies of the internal modes of TeO_6 and MoO_6 groups remain unchanged in these crystals. From IR and Raman analysis the present authors found that the two anions in phosphotellurates (*5*) and potassium sulfate tellurate (*6*) exist as independent vibrating groups without affecting each other. A detailed vibrational analysis of $Te(OH)_6 \cdot 2NH_4H_2PO_4 \cdot (NH_4)_2HPO_4$ (herein TAAP) belonging to the phosphotellurate family is made to understand the distribution of vibrational energy levels of TeO_6, PO_4, and NH_4 groups in a monoclinic lattice.

Experimental

Good quality single crystals (provided by Professor Y. F. Nicolau, France) were used. The crystals were cut in the form of rectangular parallelepipeds of size 3 × 8 × 2 mm using a method suggested for monoclinic crystals (*7*). In a monoclinic crystal such as TAAP (C_s) the A' modes are symmetric with respect to the mirror plane. They have an associated polarizability tensor of the form

$$\alpha_{A'} = \begin{bmatrix} \alpha_{xx} & 0 & \alpha_{xz} \\ 0 & \alpha_{yy} & 0 \\ \alpha_{zx} & 0 & \alpha_{zz} \end{bmatrix},$$

while the A'' modes are antisymmetric with respect to the mirror plane and have an as-

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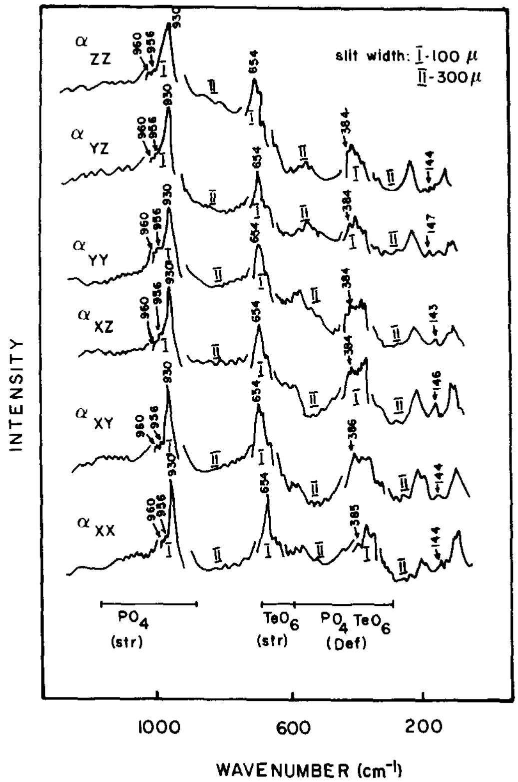

FIG. 1. Raman spectrum of $Te(OH)_6 \cdot 2NH_4H_2PO_4$ $(NH_4)_2HPO_4$ (50–1200 cm^{-1}).

sociated polarizability tensor

$$\alpha_{A''} = \begin{bmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{bmatrix}.$$

Here the polarizability tensors are defined along the xyz axes of the refractive index ellipsoid. The Raman spectra (Figs. 1 and 2) for the six polarization geometries were recorded using a SPEX Ramalog 1401 double monochromator. The green line 5145 Å of a Spectra Physics Model 165 Ar$^+$ laser was used as the excitation source, with laser power ranging from 100 to 300 mW. The IR spectrum (Fig. 3) of the polycrystalline sample was recorded in a PE 283 spectrophotometer using KBr pellet technique.

Factor Group Analysis

TAAP is monoclinic (P_n) with two formula units per unit cell (*8*). All the groups occupy general positions. There are three independent PO_4 groups with average P–O distances 1.535, 1.543, and 1.546 Å. The four ammonium groups occupy crystallographically nonequivalent C_1 sites. The vibrations of TAAP crystal may be regarded as being composed of the following vibrations:

1. Lattice vibrations, consisting of translational and rotational modes due to NH_4, PO_4, and $Te(OH)_6$ groups vibrating against each other as rigid units.
2. Internal vibrations of the PO_4^{3-} ion.

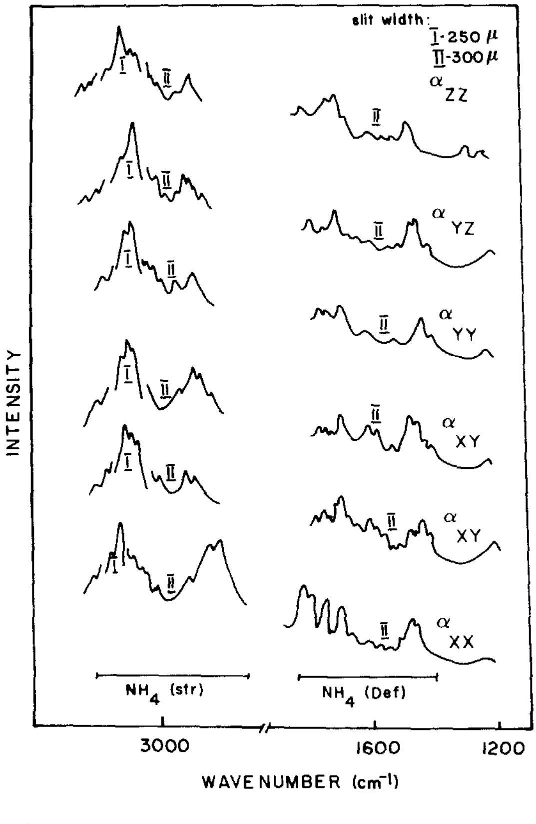

FIG. 2. Raman spectrum of $Te(OH)_6 \cdot 2NH_4H_2PO_4$ $(NH_4)_2HPO_4$ (1200–3400 cm^{-1}).

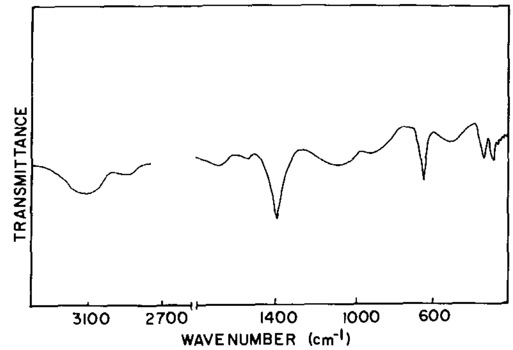

FIG. 3. IR spectrum of $Te(OH)_6 \cdot 2NH_4H_2PO_4 \cdot (NH_4)_2HPO_4$.

3. Internal vibrations of the $Te(OH)_6$ group.

4. Internal vibrations of the NH_4^+ ion.

By considering the unit cell containing two TAAP molecules, a total of 106 atoms, the standard group theoretical analysis predicts 315 fundamentals (157 A', 158 A'') at $K = 0$. All modes are IR and Raman active.

Interpretation of the Spectra

Internal Modes of PO_4^{3-} Ion

In the crystal, as the symmetry of the PO_4^{3-} ion is reduced from T_d to C_1, one can expect the appearance of IR inactive modes and the lifting of the degeneracies of the modes of the free PO_4^{3-} ion. Studies on orthophosphates (*9*) containing PO_4^{3-} ion indicate that the stretching and bending frequencies occur, respectively, in the regions 900–1200 and 300–600 cm^{-1}. The interpretation of the spectra is complicated due to the presence of different types of phosphate ions in the unit cell.

The bands belonging to different PO_4^{3-} groups may be classified on the basis of their average P–O distances. For tetrahedral ions the symmetric stretching $\nu_1(A_1)$ mode is intense in Raman and weak in IR, whereas the asymmetric stretching $\nu_3(F_2)$ is strong in both. The PO_4^{3-} ion with the shortest P–O distance (1.535 Å) is expected to give the highest frequency. Because the P–O bond distances in PO_4-II (1.543 Å) and PO_4-III (1.546 Å) are very close, there is a possibility for accidental degeneracy between the bands of these two groups. In Raman, three bands at 960, 956, and 930 cm^{-1} have been observed for the ν_1 mode of PO_4^{3-} ion in all polarization geometries. This clearly points out the possibility of resonance interaction between vibrating phosphate ions. The band at 960 cm^{-1} is assigned to the ν_1 mode of PO_4-I with the shortest bond distance. The intense band at 930 cm^{-1} is taken as the ν_1 mode of the two PO_4 groups with almost the same bond distance. The one at 956 cm^{-1} is due to the interaction between vibrating ions. The IR bands due to the three PO_4 groups appear as a broad band in the region 900–950 cm^{-1}.

All group theoretically predicted components could not be observed for the triply degenerate ν_3 mode in all orientations. As in the case of ν_1 mode, accidental degeneracy between the bands of PO_4-II and PO_4-III is expected. In all spectra this mode occupies a wide range of frequencies. The *zx* and *zy* spectra contain nine components. The additional bands are probably due to factor group splitting. The large number of PO_4^{3-} ions with different P–O distances present in the unit cell gives rise to such a large splitting (180 cm^{-1}). In IR, a broadband covering a region 1050–1150 cm^{-1} has been observed for this mode.

The bending mode of TeO_6 group falling within the range of the deformation vibrations of PO_4 group makes the identification of ν_2 and ν_4 modes difficult. Moreover accidental degeneracy is expected between the bending vibration of PO_4-II and PO_4-III groups. The Raman bands in the regions 380–450 and 470–570 cm^{-1} are due to the ν_2 and ν_4 of PO_4, respectively. In IR, due to overlapping, only very broadbands are observed. The presence of few Raman bands in the regions 700–850, 1200–1250, and 2800–2910 cm^{-1} indicates the existence of P–O(H) bonds forming HPO_4 and H_2PO_4 groups. However, in IR only a weak broadband around 2900 cm^{-1} is observed. Generally, the P–O(H) stretching vibrations are expected to be very intense in Raman. However, only very weak (Raman) bands have been observed in all polarization geometries, indicating that the hydrogen bridges are not strong enough to form HPO_4 and H_2PO_4 groups.

$Te(OH)_6$ *Groups*

The free $Te(OH)_6$ group is an octahedron with O_h symmetry. Its normal modes have five frequencies of TeO_6 corresponding to the $A_{1g} + E_g + F_{2g} + 2F_{1u}$ species and hydrogenic vibrations. The stretching and bending frequencies of TeO_6 group normally occur in the regions 580–680 and 300–400 cm^{-1}, respectively (*10*). The symmetric stretching mode $\nu_1(A_{1g})$ is observed as a very intense band at 654 cm^{-1} in all orientations. The degeneracy of the asymmetric stretching mode $\nu_2(E_g)$ is completely lifted and the Raman bands in the region 570–635 cm^{-1} are assigned to this mode. In IR a broad, medium intensity band centered at 650 cm^{-1} is observed in the Te–O stretching region (ν_1 and ν_2 modes). Because the triply degenerate asymmetric stretching mode falls in the region of the ν_4 mode of the PO_4^{3-} ion, direct observation of this vibration is not possible.

NH_4^+ *Ion Vibrations*

The unit cell contains two sets of four different ammonium ions. The coordination of ammonium hydrogens with oxygens of TeO_6 and PO_4 groups is expected to distort the structure of the ammonium ions. The N–H. . .O distances of three ammonium ions are almost equal (2.985 Å) and the other has 3.024 Å. Hence accidental degeneracies between the vibrations of three ammonium ions which have almost equal bond strengths is expected. The ν_1, ν_2, ν_3, and ν_4 modes of NH_4^+ ion under T_d symmetry appear at 3040, 1680, 3145, and 1400 cm^{-1}, respectively (*11*). Frequencies shifted from the free ion values have been observed in all orientations. The bands in the region 2925–3270 cm^{-1} are assigned to the ν_1 and ν_3 modes. The *zz* spectrum contains as many as 10 bands due to these modes. The ν_2 and ν_4 modes have been observed in the region 1400–1850 cm^{-1}. Interaction between neighboring ammonium ions and the lowering of free ion symmetry lead to the appearance of multiple bands for both stretching and bending modes. However, all group theoretically predicted bands ($36A'$, $36A''$) have not been observed because of closely spaced phonon energies.

External Modes

The bands below 300 cm^{-1} are due to external modes. Since the unit cell contains a large number of the same type of ions, the phonon energies will be closely spaced and hence all predicted number of modes could not be observed. In addition to the lattice vibrations described by the group theoretical analysis, it is possible to observe the low frequency stretching vibrations of the hydrogen bonded oxygen atoms (N–H. . .O). Since the hydrogen bonds do not occupy any symmetry positions within the crystal, the bond stretching vibrations should have both A' and A'' symmetries. This is observed for the line around 143 cm^{-1}. In addition to the fundamental $v = 0 \rightarrow v = 1$ hydrogen bond transition, it is possible to expect transitions from the excited levels. Since the hydrogen bond is highly anharmonic, these transitions would have successively lower frequencies. The intensities of these transitions decrease rapidly with increasing v. The weak intensity for the fundamental suggests that the transitions from the excited levels may not be observable. The proposed assignments are given in Table I.

TABLE I

ASSIGNMENTS OF THE OBSERVED SPECTRA

Raman (cm^{-1})						IR (cm^{-1})	Assignments^a
α_{xx}	α_{xz}	α_{yy}	α_{zz}	α_{xy}	α_{yz}		
91	72	92	98	91	92		
94	92	123	123		98		
126	96						
	121						External modes
144	146	143	144	144	147		ν(N–H. . .O)
				187			
185	206	201	202	204	207	210 w	
201	256	241	239	254	243	222 w	
231		283		269	291	235 w	
252		301				250 w	
287						262 w	
						290 m	
304	310	316	299	316	310		
316	346	342	342	324		330 m	ν_5 TeO_6
346				346	346		
364	354	356	360	358	357		
	361	363	370		361		ν_4 TeO_6
	374				376		
385	384	384	384	386	384		
439	391	401			396		ν_2 PO_4
	446				417		
514	490	478	496	498	487		
558	502	493	513	507	503	500 br	ν_4 PO_4
567	562	516	530	521	536		
		531	554	564	558		
		558					
586	584	592	587	570	576		
618	638	604	596	607	584		
632		632	631	632	603		ν_2 TeO_6
654	654	654	654	654	654	650 m	ν_1 TeO_6
708	704	729	729	708	711		
716	750	750	764	716	722		
770	786	777		750	733		Combination
				785	759		δ(Te,P)–O–H
					783		
810	820	806	809	830	830		
	849	820					ν P–O(H)
		847					
		875					
930	930	930	930	930	930		
956	956	956	956	956	956	900–950 br	ν_1 PO_4
960	960	960	960	960	960		
1006	1000	1048	1048	1066	1011		
1024	1013	1069	1034	1088	1020	1050–1150 br	ν_3 PO_4
1048	1053	1114	1098	1106	1038		
1056	1058	1139	1126	1114	1057		
1069	1071	1164	1188	1140	1073		
1086	1088	1181		1132	1096		

TABLE I—*Continued*

Raman (cm^{-1})						IR (cm^{-1})	Assignments[a]
α_{xx}	α_{xz}	α_{yy}	α_{zz}	α_{xy}	α_{yz}		
1099	1108			1187	1106		
	1152				1134		
	1180				1133		
1226	1210	1215	1236	1201	1231		β(Te,P)–O–H
			1242				
1448	1406	1423	1476	1444	1406	1400 m	
1464	1423	1456	1528	1458	1446		
1501	1446	1473	1560	1466	1542		
1557	1468	1516		1501			ν_4 NH_4
1571	1540	1538		1528			
	1582			1574			
				1590		1560 w	
1606	1602	1606	1603	1608	1621		
1672	1706	1642	1694	1648	1708		
1710	1734	1664	1725	1674	1764		
1728	1752	1719	1738	1710	1782		
1760	1764	1753	1847	1718		1700 br	ν_2 NH_4
		1768		1724			
1802		1787		1758			
1830		1810		1784			
2810	2820	2866	2909	2896	2896		
2837	2868	2899		2902			
2903	2890	2905				2900 br	Combination
		2919					ν(Te,P)–OH
	2933	2947	2947		2944		
		2986					
3008	3084	3006	3015	3000	3020		
3017	3097	3084	3031	3062	3099	3100 br	ν_1 NH_4
3024	3124	3143	3040	3084	3121		
3052	3200	3154	3070	3124	3188		ν_3 NH_4
3069		3244	3090	3182			
3114			3128	3220			
3158			3186				
3208			3206				
			3270				

[a] ν, Stretching; β, in plane bending; δ, out of plane bending.

Conclusions

(1) Resonance interaction between vibrational modes of PO_4^{3-} ions was observed.

(2) The presence of a large number of PO_4 and NH_4 groups in the unit cell causes the stretching and bending frequencies of PO_4 and NH_4 groups to occupy a wide range of spectrum.

(3) Phosphate ions exist as PO_4^{3-} ions rather than as HPO_4 and H_2PO_4 groups.

Acknowledgments

The authors are grateful to Professor Y. F. Nicolau, Cedex-France, for providing the crystals. Thanks are due to the Department of Science and Technology, India, for financial support to the authors.

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